Formation Enthalpies of Organic Compounds of Third-Row Elements from ab initio Computations

Eugene Paulechka [C, S] and Andrei Kazakov
Applied Chemicals and Materials Division, NIST, Boulder, CO, U.S.A.
yauheni.paulechka@nist.gov

The protocol for cost-effective prediction of the gas-phase enthalpies of formation [1, 2] for the compounds composed of the second-row p-elements and hydrogen has been expanded to include the third-row elements. The protocol combines the total energies of molecules from local CCSD(T)/aug-cc-pV(Q+d)Z//DF-MP2/aug-cc-pV(Q+d)Z, B3LYP-D3BJ/def2-TZVP frequencies, and the effective enthalpies of formation of atoms derived using the critically evaluated experimental enthalpies of formation. The expanded uncertainty of the predicted values is about 3 kJ×mol–1. For the new elements, a single experimental enthalpy of formation of unknown quality is typically available. Furthermore, series of consistent measurements for similar compounds often come from the same laboratory and may be a subject to systematic error.

As a result, compromise training sets considering diversity in both the functional groups present and the origins of the data were compiled. The statistical outliers were identified. Significant problems with the data quality were revealed for the silicon and phosphorus compounds. Several atomic types for different oxidation states were required to adequately describe the formation enthalpies for the phosphorus and sulfur compounds.

References

[1]. E. Paulechka; A. Kazakov. J. Chem. Theory Comput. 14 (2018) 5920-5932.

[2]. E. Paulechka; A. Kazakov. J. Chem. Eng. Data 64 (2019) 4863-4874.